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(21) International Application Number: <b>PCT/US90/01747</b> (22) International Filing Date: <b>27 March 1990 (27.03.90)</b>  (30) Priority data: 473,056                      31 January 1990 (31.01.90)      US  (60) Parent Application or Grant (63) Related by Continuation US    473,056 (CIP) Filed on                                      31 January 1990 (31.01.90)  (71) Applicant (for all designated States except US): <b>MERCK PATENT GMBH [DE/DE]; Frankfurter Strasse 250, D-6100 Darmstadt 1 (DE).</b>		(72) Inventor; and (75) Inventor/Applicant (for US only): <b>SPARROW, Robert, William [GB/US]; 28 Woodlawn Drive, Sturbridge, MA 01566 01566 (US).</b>  (74) Agents: <b>MILLEN, I., William et al.; Millen, White &amp; Zelano, Arlington Courthouse Plaza I, Suite 1201, 2200 Clarendon Boulevard, Arlington, VA 22201 (US).</b>  (81) Designated States: <b>CA, JP, US.</b>  Published <i>With international search report.</i>
(54) Title: <b>DIVALENT FLUORIDE DOPED CERIUM FLUORIDE SCINTILLATOR</b> <span style="float: right;">US 5,039,858</span>  (57) Abstract  <div style="display: flex; align-items: flex-start;"> <div style="flex: 1;"> <p>The use of divalent fluoride dopants in scintillator materials comprising cerium fluoride is disclosed. The preferred divalent fluoride dopants are calcium fluoride, strontium fluoride, and barium fluoride. The preferred amount of divalent fluoride dopant is less than about 2 % by weight of the total scintillator. Cerium fluoride scintillator crystals grown with the addition of a divalent fluoride have exhibited better transmissions and higher light outputs than crystals grown without the addition of such dopants. These scintillators are useful in radiation detection and monitoring applications and are particularly well suited for high rate applications such as positron emission tomography (PET).</p> </div> <div style="flex: 2;"> </div> </div>		

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DIVALENT FLUORIDE DOPED  
CERIUM FLUORIDE SCINTILLATOR

Field of the Invention

Scintillators are materials that emit flashes or  
5 pulses of light when they interact with ionizing  
radiation such as gamma rays. The present invention  
relates to scintillator materials comprising cerium  
fluoride. More particularly, the present invention  
relates to the use of divalent fluoride dopants in  
10 scintillator materials comprising cerium fluoride.

Background of the Invention

The use of cerium fluoride as a scintillator  
material in the detection of ionizing radiation is  
disclosed in Application Serial No. 07/218,234, filed  
15 July 12, 1988, and incorporated herein by reference.  
There, the use of cerium fluoride as a scintillator  
material in gamma ray detectors for positron emission  
tomography (PET) is also disclosed.

The value of PET as a clinical imaging technique is  
20 in large measure dependent upon the performance of the  
detectors. The typical PET camera comprises an array of  
detectors consisting of scintillator crystals coupled to  
photomultiplier tubes (PMTs). When a high energy photon  
or gamma ray strikes a detector, it produces light in the  
25 scintillator crystal that is then sensed by the PMT,  
which registers the event by passing an electronic signal  
to the reconstruction circuitry. The scintillator  
crystals themselves must have certain properties, among

which are (1) good stopping power, (2) high light yield, and (3) fast decay time.

As applied to scintillators, stopping power is the ability to stop the 511 keV photons associated with PET in as little material as possible so as to reduce the overall size of the detector, of which the scintillator crystals form a substantial portion. Stopping power is typically expressed as the linear attenuation coefficient ( $\tau$ ) having units of inverse centimeters ( $\text{cm}^{-1}$ ). After a photon beam has traveled a distance "x" in a crystal, the proportion of photons that have not been stopped by the crystal is calculated as follows:

$$\text{fraction of unstopped photons} = e^{(-\tau * x)}.$$

Thus, after traveling a distance of  $1/\tau$  (the "absorption length"), approximately 37% of the photons will not have been stopped; 63% will have been stopped. Likewise, 63% of the remaining photons will have been stopped after traveling an additional distance of  $1/\tau$ . For PET and other applications involving the detection of ionizing radiation, it is desirable for  $1/\tau$  to be as small as possible so that the detector is as compact as possible.

Light yield is also an important property of scintillators. Light yield is sometimes referred to as light output or relative scintillation output and is typically expressed as the percentage of light output from a crystal exposed to a 511 keV photon beam relative to the light output from a crystal of thallium-doped sodium iodide, NaI(Tl). Accordingly, the light yield for NaI(Tl) is defined as 100.

A third important property of scintillators is decay time. Scintillation decay time, sometimes referred to as the time constant or decay constant, is a measure of the duration of the light pulse emitted by a scintillator and is typically expressed in units of nanoseconds (nsec). As discussed in Application Serial No. 07/218,234, if a scintillator's decay constant is short, then more of its

time will be available for the detection of ionizing radiation, for example, in the case of PET, coincident photons, and the scintillator can be employed in high rate applications.

5 In addition to the three important properties discussed above, scintillator crystals should be easy to handle. For example, certain known scintillators are hygroscopic, i.e., they retain moisture, making it necessary to very tightly encapsulate them to allow their  
10 use in detectors. These hygroscopic scintillators are more difficult to use.

Prior to cerium fluoride ( $\text{CeF}_3$ ), known scintillators included (1) plastic (organic) scintillators, (2) gadolinium orthosilicate ( $\text{Gd}_2\text{SiO}_5$ , also referred to as  
15 "GSO"), (3) thallium-doped sodium iodide ( $\text{NaI(Tl)}$ ), (4) undoped cesium iodide ( $\text{CsI}$ ) and thallium-doped cesium iodide ( $\text{CsI(Tl)}$ ), (5) cesium fluoride ( $\text{CsF}$ ), (6) bismuth germanate ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , also referred to as "BGO"), and (7) barium fluoride ( $\text{BaF}_2$ ).

20 Plastic (organic) scintillators, typically composed of polystyrene doped with a wavelength-shifting additive, are commercially available under such tradenames as PILOT U and NE 111. Upon excitation with a 511 keV photon, plastic scintillators emit a light pulse having a very  
25 fast decay constant of approximately 1.5 nsec and light output proportional to the energy of the incident photon. The main disadvantage of plastic scintillators is their low density (approximately 1.1 to 1.2  $\text{g/cm}^3$ ) due to the light atoms (hydrogen and carbon) that make up the  
30 molecules of the material. Because of their low density, plastic scintillators have poor stopping power and are, therefore, poorly suited for use in PET and other applications involving the detection of ionizing radiation.

35 GSO, gadolinium orthosilicate ( $\text{Gd}_2\text{SiO}_5$ ) is a scintillator well suited for PET with good stopping power, high light yield, and reasonable decay constant.

The disadvantage of GSO is that it is very difficult to manufacture and prohibitively expensive, costing about fifty times as much as  $\text{BaF}_2$  and  $\text{CeF}_3$ , and twenty times as expensive as BGO.

5         $\text{NaI(Tl)}$ , thallium-iodide sodium iodide, has the best light output of the prior known scintillators listed above.  $\text{NaI(Tl)}$  also has reasonably good stopping power ( $1/\tau = 3.0$  cm at 511 keV). However,  $\text{NaI(Tl)}$  has a long decay constant (250 nsec), a significant disadvantage for  
10       use in PET and other time-of-flight applications.  $\text{NaI(Tl)}$  is also highly hygroscopic, making it extremely difficult to handle in that it must be encapsulated in bulky cans.

$\text{CsI(Tl)}$ , thallium-doped cesium iodide, is not  
15       particularly well suited for PET because its decay time is greater than 1000 nsec, far too long for high rate applications like PET. Undoped  $\text{CsI}$  appears suitable for PET, although its slow component is a disadvantage for high rates. This slow component can be fairly  
20       effectively removed electronically, however.

$\text{CsF}$ , cesium fluoride, has been used successfully in PET.  $\text{CsF}$  has two main disadvantages: First, it has a rather poor stopping power [absorption length ( $1/\tau$ ) =  
25       2.3 cm at 511 keV]. Second, it is extremely hygroscopic. The poor stopping power of  $\text{CsF}$  limits its ability to localize the origin of the gamma rays in PET. The hygroscopic nature of  $\text{CsF}$  makes it difficult to handle.

      BGO has the highest density ( $7.13 \text{ g/cm}^3$ ) of the prior known scintillator materials listed above. Its stopping  
30       power is the best ( $1/\tau = 1.1$  cm at 511 keV), and, as a result, BGO is best able to absorb 511 keV photons efficiently in small crystals. However, BGO's very long decay constant (300 nsec), longer even than  $\text{NaI(Tl)}$ , is a significant disadvantage for use in PET and other high  
35       rate applications involving the detection of ionizing radiation.

The use of  $\text{BaF}_2$  as a scintillator material is described in Allemand et al., U.S. Patent No. 4,510,394.  $\text{BaF}_2$  emits light having two components: a slow component having a decay constant of approximately 620 nsec and a fast component having a decay constant of approximately 0.6 nsec.  $\text{BaF}_2$  has a light yield of approximately 16% that of  $\text{NaI(Tl)}$  and about half the stopping power of BGO ( $1/\tau = 2.3 \text{ cm at } 511 \text{ keV}$ ). Unlike  $\text{CsF}$  and  $\text{NaI(Tl)}$ ,  $\text{BaF}_2$  is not hygroscopic.

The fast component of  $\text{BaF}_2$  emits light in the ultraviolet region of the spectrum. Glass photomultiplier tubes are not transparent to ultraviolet light, so a quartz photomultiplier tube must be used to detect the fast component of  $\text{BaF}_2$ . Since quartz photomultiplier tubes are substantially more expensive than glass (by a factor of two), one would prefer to avoid using  $\text{BaF}_2$ , if possible, in favor of using a scintillator that can be detected by a glass photomultiplier tube. The fast component gives  $\text{BaF}_2$  very good timing resolution, but the slow component limits its high rate capabilities. In other words, it takes  $\text{BaF}_2$  longer to get ready for the next event. (This slow component can be fairly effectively removed electronically, however).

Of the prior known scintillator materials, BGO has the best stopping power,  $\text{NaI(Tl)}$  has the best light yield, and  $\text{BaF}_2$  has the best timing resolution. However, as noted above, some of these known materials have significant shortcomings which hinder their performance as scintillators for PET and other applications involving the detection of ionizing radiation: BGO has a very long decay constant;  $\text{NaI(Tl)}$  also has a very long decay constant and is hygroscopic. Of these materials,  $\text{BaF}_2$  has the best balance of stopping power, light output, and decay constant and does not present a problem with hygroscopy. However, the slow component of  $\text{BaF}_2$  does limit its rate capabilities.

As disclosed in Application Serial No. 07/218,234, cerium fluoride,  $\text{CeF}_3$ , has been found to provide a balance of stopping power, light yield, and decay constant that is superior to previously known scintillator materials.

5 As a result, cerium fluoride is favorably suited for use as a scintillator in positron emission tomography and other applications involving the detection of ionizing radiation. The relevant properties of  $\text{CeF}_3$ , as compared to those of prior known scintillator materials, are shown  
10 in Figure 1.

As shown in Figure 1,  $\text{CeF}_3$  provides a balance of stopping power, light yield, and decay constant that is superior to other known scintillator materials. In particular,  $\text{CeF}_3$  exhibits a fast component of  
15 approximately 5 nsec and a low component having a decay constant of approximately 30 nsec, both far superior to those of  $\text{NaI(Tl)}$  and BGO. With respect to light yield,  $\text{CeF}_3$  exhibits a value of 4-5% that of  $\text{NaI(Tl)}$ ; its light yield is thus about one-half that of BGO. In addition,  
20 the absorption length (stopping power) of  $\text{CeF}_3$  ( $1/\tau = 1.9$  cm at 511 keV) is between that of BGO and  $\text{BaF}_2$ . Finally,  $\text{CeF}_3$  is superior in that its decay constant is far shorter; and it is not hygroscopic, making it much easier to handle than  $\text{NaI(Tl)}$ .

25 As further shown in Figure 1, in contrast to  $\text{BaF}_2$ ,  $\text{CeF}_3$  has superior stopping power ( $1/\tau$ ) but inferior light yield. In addition,  $\text{CeF}_3$  has a fast component like  $\text{BaF}_2$ . Moreover, while the fast component of  $\text{BaF}_2$  can only be detected using expensive quartz photomultiplier tubes,  
30 the fast component of  $\text{CeF}_3$  can be detected using much less expensive glass photomultiplier tubes. Finally, as shown in Figure 1, in contrast to BGO,  $\text{CeF}_3$  has inferior absorption length (stopping power) and light yield, but has a decay constant far superior to that of BGO. Thus,  
35  $\text{CeF}_3$  provides adequate stopping power and light yield with an improved decay constant.



In developing a commercial grade  $\text{CeF}_3$  scintillator, the main objectives are to produce high quality  $\text{CeF}_3$  scintillators reliably and at low cost. If possible, it is desirable to produce large crystals of uniformly clear, scatter-free  $\text{CeF}_3$ , while avoiding the use of extremely pure and thus expensive  $\text{CeF}_3$  as a starting material. The use of extremely pure  $\text{CeF}_3$  is prohibitively expensive on a commercial scale because of the difficulty in purifying  $\text{CeF}_3$  in large quantities. Thus, if lower purity  $\text{CeF}_3$  could be employed as a starting material, there would be a substantial reduction in the cost of producing cerium fluoride scintillators on a commercial scale.

#### Objects of the Invention

It is, therefore, an object of the invention to provide high quality cerium fluoride scintillator crystals reliably and at low cost.

Another object of the invention is to produce large crystals of uniformly clear, scatter-free cerium fluoride, while avoiding use of extremely pure cerium fluoride as a starting material.

A further object of the invention is to provide an economical method of producing high quality cerium fluoride scintillator crystals in large quantities.

#### Summary of the Invention

The above objects are accomplished by a scintillator material comprising cerium fluoride and a divalent fluoride dopant. The preferred divalent fluoride dopants are calcium fluoride, strontium fluoride, and barium fluoride. The preferred amount of divalent fluoride dopant is less than about 2% by weight of the total scintillator.

The method of preparing the improved cerium fluoride scintillator comprises adding a scintillation-enhancing divalent fluoride dopant, preferably in the form of

calcium fluoride, strontium fluoride, or barium fluoride, and preferably in an amount less than about 2% by weight of the total scintillator.

#### Brief Description of the Drawings

5           Figure 1 is a table showing the relevant properties of  $\text{CeF}_3$  to those of prior known scintillator materials.

          Figure 2 is a graph showing the amount of light transmitted and emitted upon excitation with 254 nm ultraviolet light, by wavelength, of extremely pure  $\text{CeF}_3$  at room temperature.

10           Figure 3 is a graph showing the scintillation intensity as a function of time (decay curve) for extremely pure  $\text{CeF}_3$ , taken with a quartz photomultiplier tube at room temperature.

15           Figure 3 is a graph showing the scintillation intensity as a function of time (decay curve) for extremely pure  $\text{CeF}_3$ , taken with a quartz photomultiplier tube at room temperature.

          Figure 4 is a graph showing the scintillation intensity as a function of time (decay curve) of the slow component of extremely pure  $\text{CeF}_3$  at room temperature.

          Figure 5 is a graph showing the scintillation intensity as a function of time (decay curve) of the fast component of extremely pure  $\text{CeF}_3$  at room temperature.

25           Figure 6 is a graph showing the scintillation intensity as a function of time (decay curve) on a linear scale of the slow and fast components of extremely pure  $\text{CeF}_3$  at room temperature.

          Figure 7 is a graph showing the amount of light transmitted by wavelength of 99% pure  $\text{CeF}_3$  starting material doped with 0.5%  $\text{CaF}_2$  and the amount of light emitted upon excitation with 254 nm ultraviolet light, by wavelength, of two samples doped with 0.5%  $\text{CaF}_2$  and 0.5%  $\text{BaF}_2$ .

35           Figure 8 is a graph showing the scintillation intensity as a function of time (decay curve) for 99%

pure  $\text{CeF}_3$  starting material doped with 0.5%  $\text{BaF}_2$ , taken with a quartz photomultiplier tube at room temperature.

Figure 9 is a graph showing the scintillation intensity as a function of time (decay curve) for 99% pure  $\text{CeF}_3$  starting material doped with 0.5%  $\text{BaF}_2$ , taken with the addition of a glass filter to the quartz photomultiplier tube at room temperature.

#### Detailed Description of the Drawings

As discussed above, Figure 1 is a tabulation of the relevant properties of  $\text{CeF}_3$  as compared to those of prior known scintillator materials. As shown in Figure 1,  $\text{CeF}_3$  falls between BGO and  $\text{BaF}_2$  with respect to properties such as density ( $6.16 \text{ g/cm}^3$ ), absorption length at 511 keV (1.9 cm), and index of refraction (1.68). Like  $\text{BaF}_2$ ,  $\text{CeF}_3$  has at least two emission components with decay times of approximately 5 nsec and 30 nsec. Although the fast component of  $\text{CeF}_3$  is not as fast as the fast component of  $\text{BaF}_2$ , its slow component is a factor of 20 times faster than the slow component of  $\text{BaF}_2$  and a factor of 10 faster than BGO. The amount of light emitted by  $\text{CeF}_3$  is approximately 50% that of BGO and about the same order of magnitude as the fast component of  $\text{BaF}_2$ . A timing resolution for a single  $\text{CeF}_3$  PET crystal of 0.56 nsec has also been achieved.

Turning next to Figure 2, the emission and transmission intensities are plotted as a function of wavelength for extremely pure  $\text{CeF}_3$  at room temperature; but, as will be discussed in more detail below, there are actually two components of this emission. In comparing the light output with a quartz and a glass PMT, the quartz PMT gave about 15% greater signal. If there is a reason to detect this small addition of light output, a UV-glass PMT can be used, which adds little to the cost of the photodetector.

The scintillation intensity as a function of time (decay curve) for extremely pure  $\text{CeF}_3$ , taken with a quartz

photomultiplier tube at room temperature is shown in Figure 3. It is evident from Figure 3 that there is more than one decay constant present. A simple fit yields a decay constant of 26.9 nsec.

5 To separate the components of the decay spectrum, a glass filter (with a cutoff at about 330 nm) was placed over the face of the quartz PMT. This filter combination removes much of the fast component, somewhat more than would be removed by a glass PMT alone. This decay curve  
10 was normalized to the quartz PMT decay curve of Figure 3 at long scintillation times and subtracted from Figure 3. Since the spectrum that remains corresponds to the bluest light and is, therefore, associated with the short decay component, a decay curve with only the fast component is  
15 thus generated. The latter curve is then renormalized such that it equals the apparent residual fast component from the glass filter curve. The result of this subtraction, which yields the decay curve for the slow component of extremely pure  $\text{CeF}_3$  at room temperature, is  
20 shown in Figure 4. Figure 4 is well fit by a single decay constant of 30.3 nsec.

The decay curve for the fast component of extremely pure  $\text{CeF}_3$  at room temperature results from the subtraction of Figure 4 from Figure 3 and is shown in Figure 5.  
25 Figure 5 can be fitted with two decay constants of 5.0 and 8.7 nsec. The longer decay constant may represent a third component to the decay, or it may simply be an artifact of the technique used to separate the decay constants. Figure 6 shows the fast and slow components  
30 of extremely pure  $\text{CeF}_3$  on a linear scale. At room temperature, the fast component of  $\text{CeF}_3$  produces about 33% of the scintillation.

As stated above, divalent fluorides added in amounts less than about 2% by weight of the total scintillator  
35 have proven useful in the growing of clear material. Examples of such divalent fluorides are  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$ .  $\text{CeF}_3$  scintillator crystals grown with the addition

of a divalent fluoride have exhibited better transmissions and higher light outputs than crystals grown without the addition of such dopants.  $\text{CaF}_2$  is the most preferred dopant, presumably because it has a  
5 lattice size that is similar to that of  $\text{CeF}_3$ . The amount of additive necessary depends on the purity of the starting material.

In attempting to reduce the cost of producing commercial grade  $\text{CeF}_3$ , the use of less than extremely pure  
10 starting materials is preferred. In this regard, starting materials of only 99% pure  $\text{CeF}_3$  were employed, with the remaining 1% consisting primarily of other rare earth elements such as  $\text{DyF}_3$ ,  $\text{EuF}_3$ ,  $\text{GdF}_3$ , and  $\text{SnF}_3$ . The  
15 term "rare earth" is a misnomer in that they are not rare; their expense is due primarily to the difficulty in their purification. If such comparatively low purity starting materials can be employed in the preparation of commercial grade scintillators, there would be a  
substantial reduction in production costs.

20 Good transmissions have been achieved with the addition of a small amount of divalent fluoride to the 99% pure  $\text{CeF}_3$  starting material. Figure 7 shows the transmission spectrum of 99% pure  $\text{CeF}_3$  starting material doped with 0.5%  $\text{CaF}_2$ . The sharp cutoff at short  
25 wavelengths is typical in 99% pure  $\text{CeF}_3$  doped with other divalent fluorides. Figure 7 also shows the emission spectra (excited with 254 nm ultraviolet light) of two samples, one doped with 0.5%  $\text{CaF}_2$  and the other doped with  
0.5%  $\text{BaF}_2$ . The  $\text{BaF}_2$  doped material exhibited an emission  
30 spectrum that differed significantly from that of pure  $\text{CeF}_3$ ; the emission spectrum of the  $\text{CaF}_2$  doped material differed less significantly from that of extremely pure  $\text{CeF}_3$ . Both samples showed a reduction in light output of  
about 37% less than the light output from a sample  
35 prepared from extremely pure starting material.

Figure 8 shows the decay curve of the sample doped with 0.5%  $\text{BaF}_2$ , taken with a quartz PMT at room

temperature. In comparison to Figure 3, Figure 8 exhibits a much higher fraction of the signal in the fast component.

5 The decay curve shown in Figure 9 was obtained with the addition of a glass filter. In comparison to Figure 6, which is similar to the raw data for the extremely pure  $\text{CeF}_3$  crystal using the glass filter, it is evident that much more of the fast component remains. The fast component is thus shifted toward the longer wavelengths.  
10 The decay curves for the  $\text{CaF}_2$  doped material was almost indistinguishable from those resulting from  $\text{BaF}_2$  doped material.

The results of the analysis of the decay spectrum of the 99% pure  $\text{CeF}_3$  material confirm that all of the 37%  
15 reduction in light output is due to the slow component of the emission. By combining the fast component of the extremely pure  $\text{CeF}_3$  (Figure 5) with 45% of its slow component (see Figure 4), the resulting decay spectrum was found to be almost identical to the decay spectra of  
20 the 99% pure  $\text{CeF}_3$  doped with either  $\text{CaF}_2$  or  $\text{BaF}_2$ . These results are analogous to the behavior noted for  $\text{BaF}_2$  scintillators, where the addition of a small concentration of dopant, such as Tm or La, causes a substantial reduction in the slow component while having  
25 little effect on the fast component.

In view of the foregoing, a divalent fluoride doped cerium fluoride scintillator is provided having good stopping power and favorable mechanical properties. Among its most important advantages over prior known  
30 scintillators are its very fast decay constants of approximately 5 nsec and 30 nsec, without the very long component (sometimes several hundred nanoseconds) of other scintillators.

The cerium fluoride scintillators described herein  
35 are useful in nuclear physics applications and in applications involving radiation detection and monitoring and are particularly well suited for high rate

applications such as positron emission tomography (PET). Cerium fluoride scintillators are also useful in applications having high background signals, and these scintillators may also be useful in applications such as the detection of the 10.8 MeV nitrogen gamma line in explosive materials.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

The entire disclosures of all applications, patents and publications, cited above and below, are hereby incorporated by reference.

20

## EXAMPLES

### Example 1: Procedure

Doped  $\text{CeF}_3$  crystals are grown by the Stockbarger technique, as described in U.S. Patent No. 2,214,976.

According to that procedure, a vacuum system is provided comprising a base plate, bell jar, diffusion pump, and backing pump. Installed inside the bell jar is a graphite heating system consisting of a side heater, grid heater, inner cylinder, and outer cylinder. Power is fed to the heaters via vacuum tight leadthrough electrodes in the base plate. Power to the furnace is controlled by a silicon-controlled rectifier power controller. Extending through the center of the base plate is a support shaft that can be raised or lowered by means of a motor-driven lead screw.

To grow doped  $\text{CeF}_3$ , the capacity of a growth crucible is established, and the correct ratio of powders of  $\text{CeF}_3$  and dopant are weighed on a precision balance. The powders are intimately mixed and loaded into a growth crucible manufactured from graphite. The crucible is closed with a graphite lid. One or several crucibles are placed on top of the support shaft. The heaters are assembled around it or them and the bell jar is lowered. The system is evacuated, and sufficient power is supplied to the furnace to melt the materials. The dropping motor is then activated so as to cause the crucible to be lowered.

As the crucible is lowered down the temperature gradient in the furnace, the tip of the crucible or a seed crystal cools below the melting point and solidifies. After all of the material is solidified, the power is reduced, the resultant crystal is annealed, and then slowly cooled to room temperature. The system is then brought back to atmospheric pressure and the crystal(s) removed.

Generally,  $\text{CeF}_3$  crystals can be grown by first putting into the growth crucible a "seed" crystal made from a piece of single crystal  $\text{CeF}_3$ . The powders of  $\text{CeF}_3$  and dopant are then placed on top of the seed. The growth procedure is as described above but, with judicious positioning, the powder can be controlled to melt the powder without melting the seed crystal. When this is done, the resultant  $\text{CeF}_3$  crystal will have the orientation of the original seed crystal.

#### Example 2

8.89 g of  $\text{BaF}_2$  and 1000 g of  $\text{CeF}_3$  is thoroughly mixed by shaking them together in a sealed container. The mixture is then poured into a growth crucible or into a crucible in which an orientation "seed" has been placed in a seed pocket machined in the tip of the crucible.



The crucible is then closed, evacuated, and heated according to the procedures set forth in Example 1.

Using this procedure, there is obtained  $\text{CeF}_3$  crystals doped with 1 mol% of  $\text{BaF}_3$ .

5     Example 3

3.96 g of  $\text{CaF}_2$  and 1000 g of  $\text{CeF}_3$  is thoroughly mixed by shaking them together in a sealed container. The resultant mixture is then poured into a growth crucible or into a crucible in which an orientation "seed" has  
10     been placed. The crucible is then sealed, evacuated, and heated in accordance with the procedure set forth in Example 1.

Using this procedure, there is obtained  $\text{CeF}_3$  crystals doped with 1 mol% of  $\text{CaF}_2$ .

15     Example 4

6.37 g of  $\text{SrF}_2$  and 1000 g of  $\text{CeF}_3$  is thoroughly mixed by shaking them together in a sealed container. The mixture is then poured into a growth crucible or into a crucible in which an orientation "seed" has been placed.  
20     The crucible is then sealed, evacuated, and heated in accordance with the procedure set forth in Example 1.

This procedure yields  $\text{CeF}_3$  crystals doped with 1 mol% of  $\text{SrF}_2$ .

The preceding examples can be repeated with similar  
25     success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of  
30     this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

WHAT IS CLAIMED IS:

1. A scintillator comprising cerium fluoride and a divalent fluoride dopant, said scintillator having a fast component with a decay constant of about 5 nanoseconds and a slow component with a decay constant of about 30 nanoseconds.

2. The scintillator of claim 1, wherein said dopant is calcium fluoride.

3. The scintillator of claim 1, wherein said dopant is strontium fluoride.

4. The scintillator of claim 1, wherein said dopant is barium fluoride.

5. The scintillator of claim 1, wherein said dopant is present in an amount less than about 2% by weight of the total scintillator.

6. A scintillator comprising cerium fluoride and a scintillation-enhancing dopant represented by the formula  $\text{XF}_2$ , wherein X is selected from the group consisting of calcium, strontium, and barium.

7. The scintillator of claim 6, wherein said dopant is present in an amount less than about 2% by weight of the total scintillator.

8. A method of preparing a scintillator comprising cerium fluoride comprising adding a scintillation-enhancing divalent fluoride dopant.

9. The method of claim 8, wherein said dopant is calcium fluoride.

10. The method of claim 8, wherein said dopant is strontium fluoride.

11. The method of claim 8, wherein said dopant is barium fluoride.

12. The method of claim 8, wherein said dopant is added in an amount less than about 2% by weight of the total scintillator.

13. A cerium fluoride crystal doped with calcium fluoride.

14. The cerium fluoride crystal of claim 13, wherein the calcium fluoride is present in an amount of less than about 2% by weight of the crystal.

15. A cerium fluoride crystal doped with strontium fluoride.

16. The cerium fluoride crystal of claim 15, wherein the strontium fluoride is present in an amount of less than about 2% by weight of the crystal.

17. A cerium fluoride crystal doped with barium fluoride.

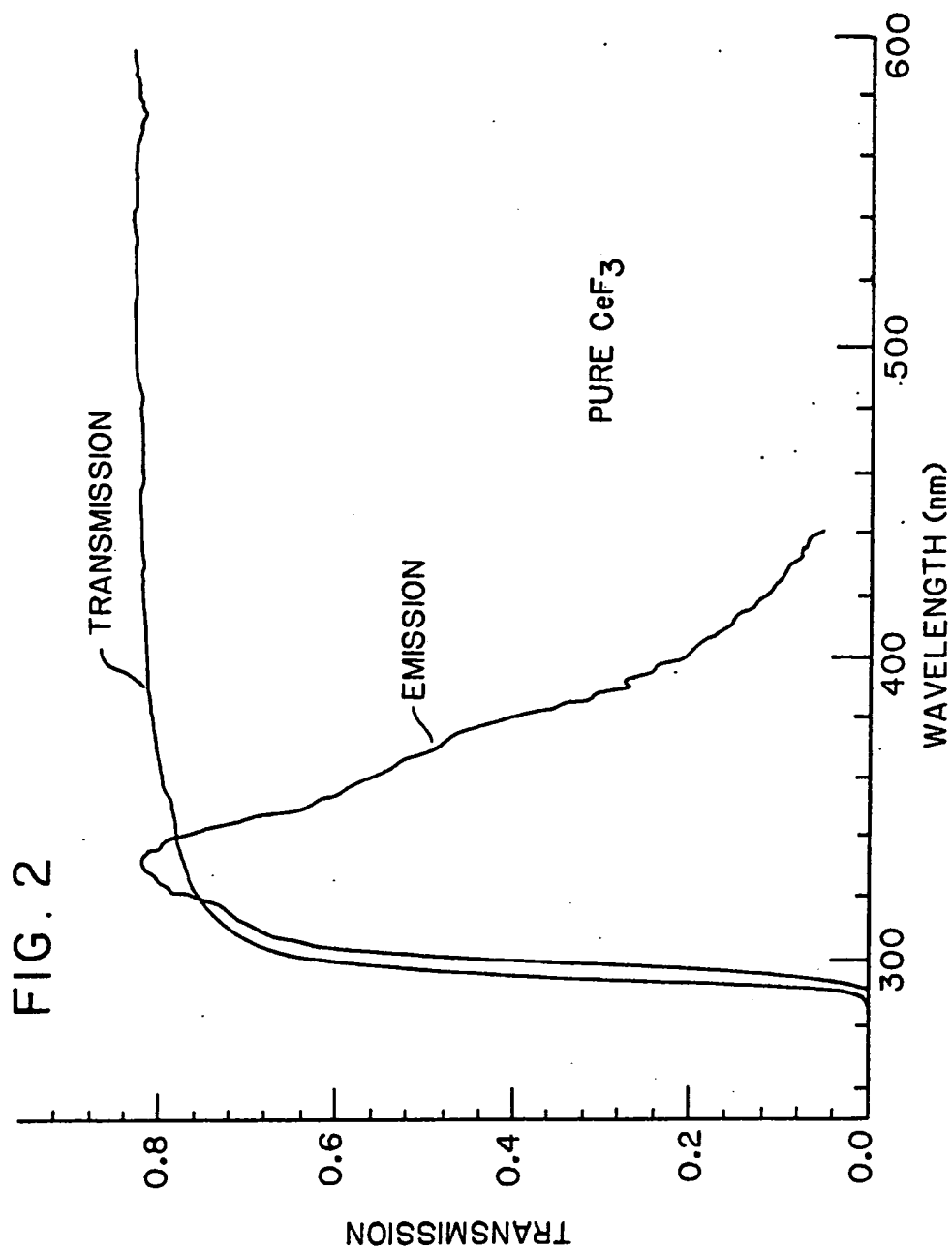
18. The cerium fluoride crystal of claim 17, wherein the barium fluoride is present in an amount of less than about 2% by weight of the crystal.

## PROPERTIES OF VARIOUS INORGANIC SCINTILLATORS

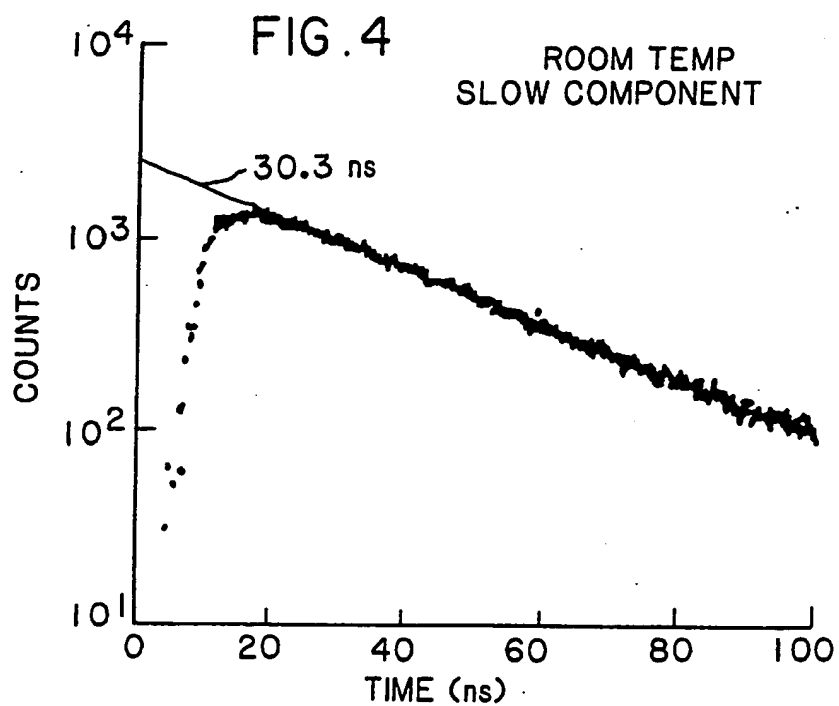
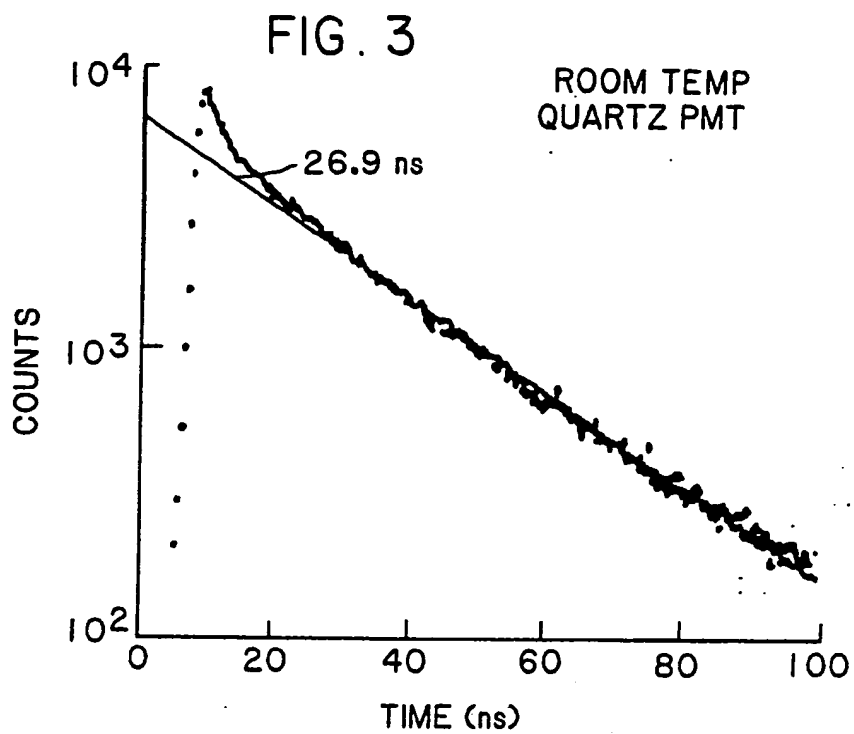
	CeF3(1)		BaF2(3)		BGO(4)		CsF(4)		CsI(5-7)		CsI(TD)(4,7)		NaI(TD)(4,8)		GSO(9)	
DENSITY	6.16		4.9		7.13		4.64		4.53		4.53		3.67		6.71	
ABSORPTION LENGTH (1/e in cm, AT 511 keV)	1.9		2.3		1.1		2.3		1.8		1.8		2.9			
RADIATION LENGTH (cm)	1.7		2.1		1.1		2.0		1.86		1.86		2.6			
DECAY CONSTANT - SHORT $\approx$ 5			0.6		300		2.8		$\approx$ 10,36		> 1000		230		60	
(n sec) - LONG 30			620				4.4		> 1000				150ms			
PEAK EMISSION - SHORT 310			220		480		390		300		550		415		430	
- LONG 340			310						> 400							1/6
INDEX OF REFRACTION	1.68		1.56		2.15		1.48		1.8		1.8		1.85		1.9	
AT PEAK EMISSION																
LIGHT YIELD	4-5		5		7-10		6		3.7		85		100		20	
[NaI (TD) $\equiv$ 100]			16													
HYGROSCOPIC	NO		SLIGHT		NO		VERY		SLIGHT		SLIGHT		YES		NO	
PROBLEMS FOR PET			q PMT		SLOW		HYG.		uv gl. PMT		SLOW		SLOW		COST	
			SLOW COMP.				COST		SLOW COMP.							

FIG. 1

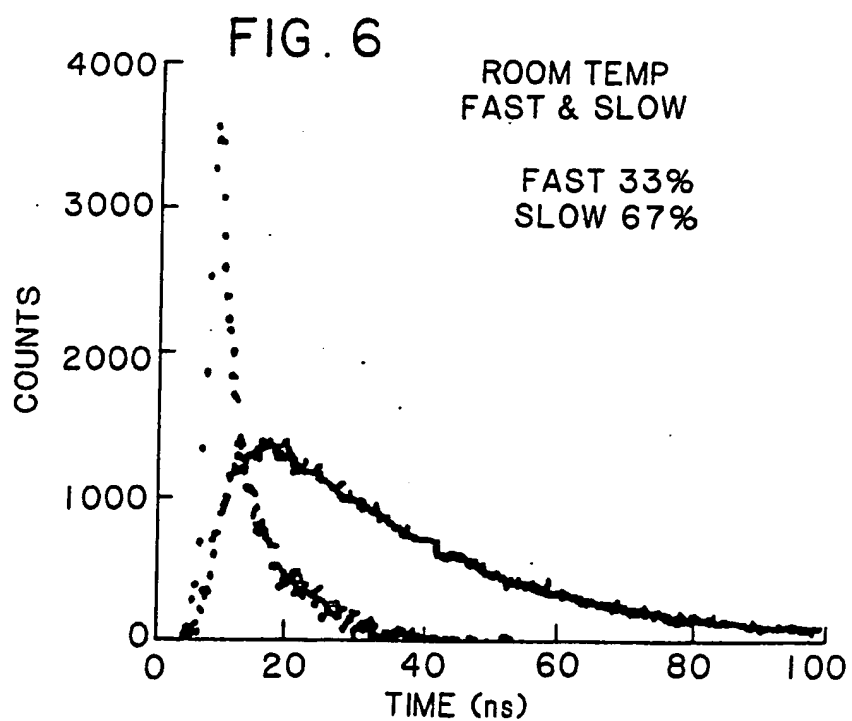
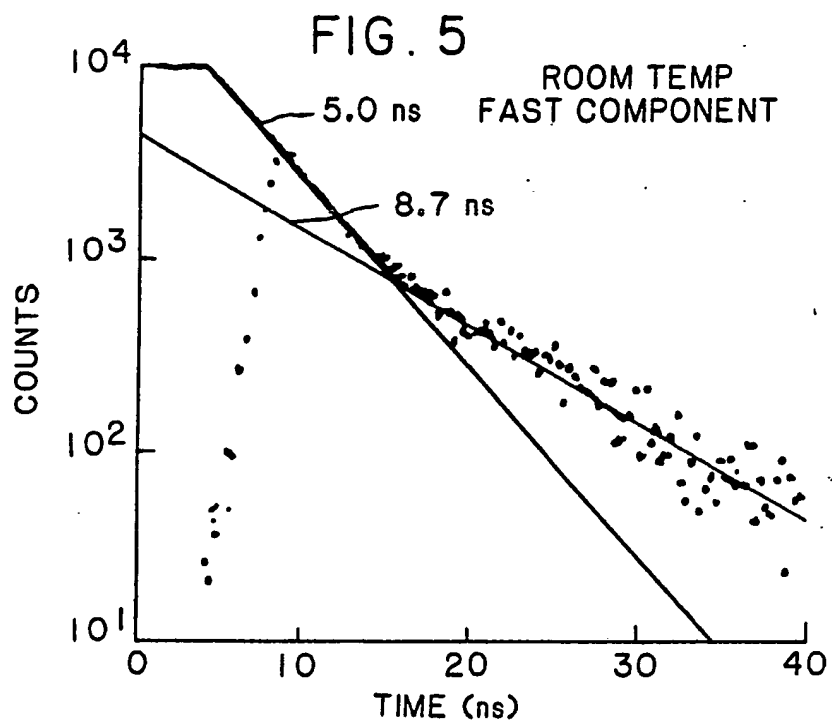
2/6



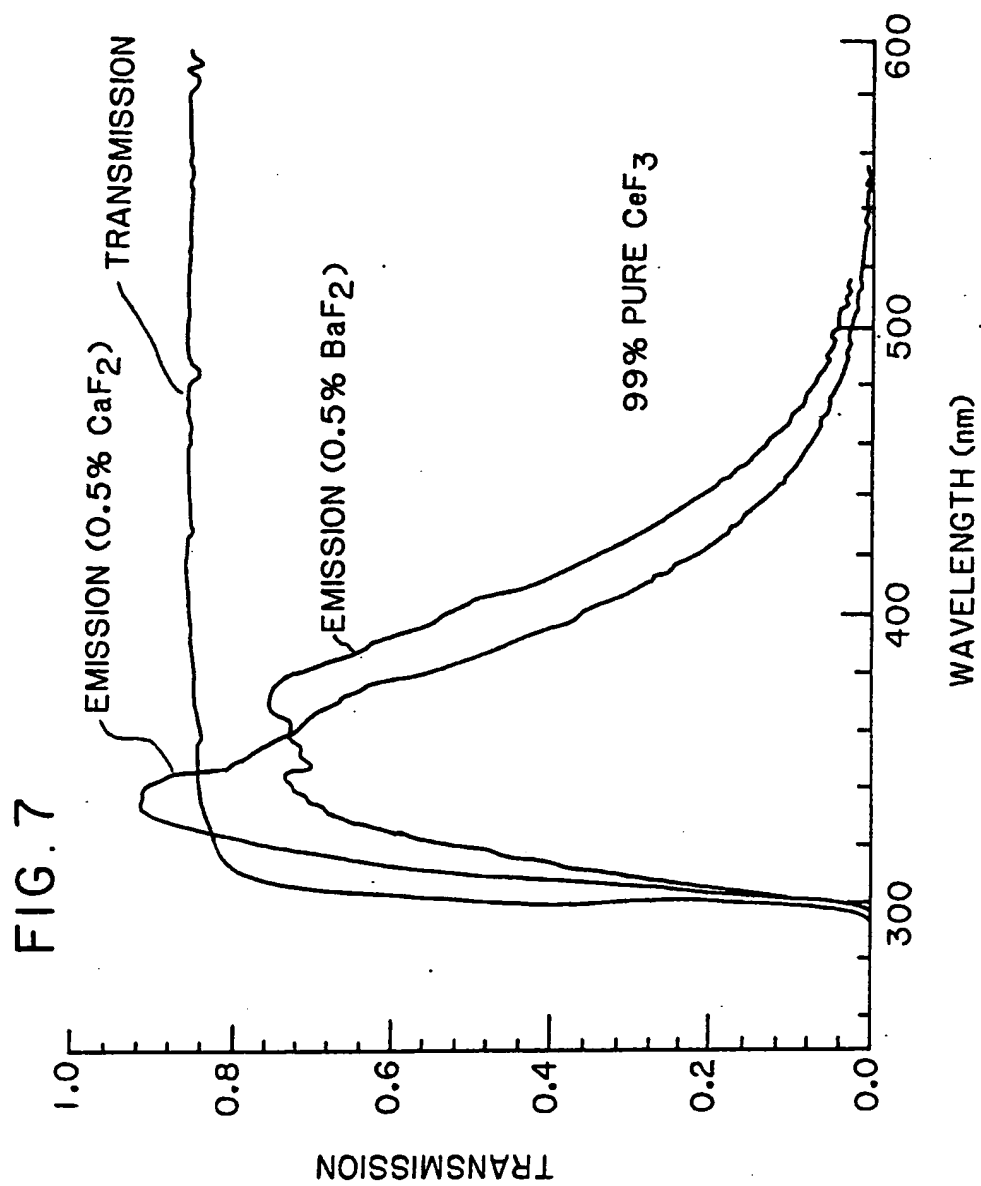
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4/6

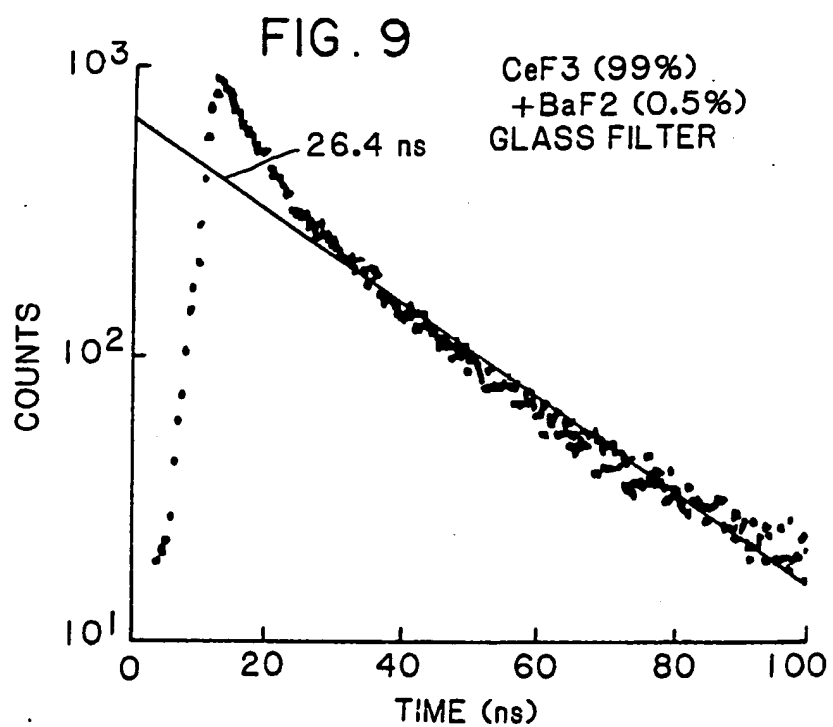
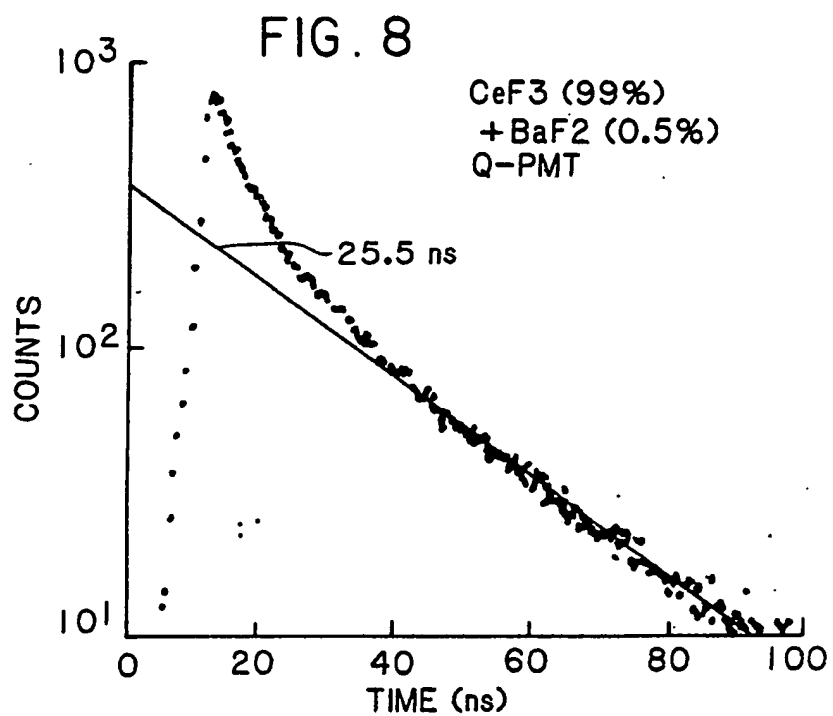


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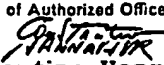


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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/01747

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. <sup>3</sup> G 01 T 1/202 . . . . . U.S. 250/363.03		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
US	250/363.03, 252/301.4H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 4,510,394 (ALLEMAND <i>ET AL.</i> ) 09 APRIL 1985 (09.04.85).)	1-18
A	US, A, 2,214,976 (STOCKBARGER) 17 SEPTEMBER 1940 (17.09.40).)	1-18
A	<i>The Journal of Chemical Physics</i> , Volume 51, no. 8, issued 1969, 15 October, G. Blasse and A. Bril, 'Energy Transfer in TB <sup>3+</sup> -Activated Cerium(III) Compounds', pages 3252-3254.)	1-18
[List ends.]		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
26 OCTOBER 1990		12 FEB 1991
International Searching Authority		Signature of Authorized Officer
ISA/US		 Constantine Hannaher